STUDIES IN THE ISOFLAVONE SERIES

BY
ROBERT WHISMAN STEPHENSON
A.B., Indiana University, 1938

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1942

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Introduction

Isoflavone structure (3-phenylbenzo-8-pyrone) has been assigned to a number of naturally occurring compounds. One degradation method used in deducing this structure involves cleavage by alkali. Some isoflavones yield a resorcinol derivative, formic acid, and a substituted desoxybenzoin; others give a substituted α-toluic acid in place of the desoxybenzoin. In the present work, a number of isoflavones with hydroxyl groups in different positions and the degradation of each of these by alkali was studied in order to determine just what structures are necessary in order that α-toluic acid may be a degradation product.

One of the natural glucosides occurring in *Iris tectorum* is tectoridin. Its aglucone, tectorigenin, has one of four isomeric structures[1,6] : *a*) 4,6-dihydroxy-5-methoxy-2-(*p*-hydroxybenzyl)-coumaran-3-one *b*) 4,6-dihydroxy-7-methoxy-2-(*p*-hydroxybenzyl)-coumaran-3-one *c*) 5, 7, 4′-trihydroxy-6-methoxyisoflavone *d*) 5,7,4′-trihydroxy-8-methoxyisoflavone. The coumaran structures have been shown to be improbable. The second purpose of the present investigation was to synthesize by known reactions the dimethyl ether of structure *c*) and compare this synthetic product with the corresponding derivative from natural tectorigenin.

Discussion of Results

Isoflavone,[4] 7-hydroxy-2-methylisoflavone,[2] 5,7-dihydroxy-2-methylisoflavone,[2] and 4′-hydroxyisoflavone were synthesized by methods similar to those previously described by other investigators. On dilute alkaline cleavage each of these isoflavones except 5,7-dihydroxy-2-methylisoflavone gave the corresponding desoxybenzoin. On alkaline fusion: isoflavone gave salicylic acid and *p*-cresol; 7-hydroxy-2-methylisoflavone gave resorcinol and toluene; 5,7-dihydroxy-2-methylisoflavone gave

∝-toluic acid and phloroglucinol. These results are experimental confirmation of Walz's[7] suggestion that a hydroxyl in position 5 is necessary before ∝-toluic acid is formed on alkaline cleavage of an isoflavone.

The condensation of 4,5-dimethoxyresorcinol[3] with homoanisonitrile was affected by a Hoesch type reaction to give 3,4-dimethoxy-2,6-dihydroxy-∝-(*p*-methoxyphenyl)-acetophenone. The latter on treatment with powdered sodium and ethyl formate gave 6,7,4′-trimethoxy-5-hydroxyisoflavone. This compound and the acetate prepared from it were found to be identical by analyses and mixed melting points with the corresponding compounds prepared by Matson[5] from natural tectorigenin.

Summary

Four isoflavones have been synthesized, and their alkaline degradation studied. The products obtained give experimental confirmation to Walz's[7] suggestion that a hydroxyl in position 5 is necessary before ∝-toluic acid is obtained on alkaline cleavage of an isoflavone.

The dimethyl ether of tectorigenin has been synthesized by known reactions and found to be identical with the dimethyl ether prepared from natural tectorigenin. This synthesis established the structure of tectorigenin.

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VITA

The author was born in Adams County, Indiana on November 15, 1915. He attended public schools in northern Indiana and graduated from Bourbon Township High School in 1933. In the fall of 1934, he entered Indiana University, Bloomington, Indiana, and received a degree, Bachelor of Arts, in June, 1938. In the fall of 1938 he entered the Graduate School at the University of Illinois where he was Assistant in Chemistry for four years.

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